The symmetry of helical chains

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Abstract
In crystals, polymeric chain molecules often adopt helical structures. Neglecting small distortions possibly caused by an anisotropic environment within the crystal, the symmetry of the single helix can by described by a rod group, which has translational symmetry in one dimension. The rod groups obtain Hermann–Mauguin symbols similar to space groups, beginning with a script style $\mathcal{p}$ followed by a screw axis symbol; the order of the screw axis can adopt any value. In a crystal, the rod-site symmetry, the so-called penetration rod group, must be a common crystallographic rod subgroup of the molecular rod group and the space group. Instructions are given for the derivation of the rod subgroups in question for a helical rod group of any order. In polymer chemistry, a helix is designated by a (chemical) symbol like 7/2, which means 7 repeating units in two coil turns of covalent bonds per translational period. The corresponding Hermann-Mauguin screw axis symbol is easily derived with a simple formula from this chemical symbol; for a 7/2 helix it is 7_3 or 7_4, depending on chirality. However, it is not possible to deduce the chemical symbol from the Hermann-Mauguin symbol, because it depends on where the covalent bonds are assumed to exist. Covalent bonds are irrelevant for symmetry considerations; a symmetry symbol does not depend on them. A chemically right-handed helix can have a left-handed screw axis. The derivation of the Hermann-Mauguin symbol of a multiple helix is not that easy, as it depends on the mutual orientation of the interlocked helices; conversion formulas for simpler cases are presented. Instead of covalent bonds, other kinds of linking can serve to define the chemical helix, for example, edge- or face-sharing coordination polyhedra.

1. Introduction[1]

When polymeric chain molecules crystallize, they adopt a symmetrical conformation. Within the crystal, the molecule has a site symmetry that must be compatible with the crystal's space group. However, the single (isolated) molecule often has a higher symmetry to a good approximation. For non-polymeric molecules we describe this ideal symmetry using the Schoenflies or Hermann-Mauguin symbol of a point group. For example, we say a benzene molecule to have the (point) symmetry D_{6h} or 6/*mmm*, even if, strictly speaking, the molecule has only the symmetry C_i ($\bar{1}$) required by its site symmetry in the space group *Pbca* in crystalline benzene; that is and must be a subgroup of D_{6h} (provided there is no misorder).

When we describe the symmetry of a single molecule, we act as if it would be located in an isotropic surrounding, although this is never really true in the crystalline state. This applies even if it is a molecular ion, which is actually surrounded by nearby counter ions. From the chemical point of view, this inaccuracy may be neglected almost always. From experience we know that the shape of a molecule in a crystal, as a rule, deviates only marginally from that of the free molecule. However, significant deviations are possible for conformation angles and when molecules associate or form ionic structures during the crystallization process (for example, $Al_2Cl_6(g) \rightarrow (AlCl_3)_\infty(s)$ layers or $N_2O_5(g) \rightarrow NO_2^+NO_3^-(s)$).

The following considerations deal with polymeric molecules having translational symmetry in only one dimension, based on structures determined by crystallographic methods. We do not deal with biomolecules, nano tubes, inclusion compounds, supramolecular structures, liquid crystals, framework structures having helical components (*e.g.* quartz), helical magnetic structures or helical spin density waves.

2. Terminology

Because in the literature some terms are used with changing or unclear meanings, in the following we define a few terms such as we mean them here.

Polymer main chain. Strand of atoms, held together by a continuous sequence of covalent bonds.

Symmetry. Property of a body, whose building blocks are mapped exactly onto one another by a mathematical prescription. In crystallography, this prescription is strictly complied with. As usual in chemistry, we are content with a good approximation. However, we do not do this as liberally as it is common when describing the symmetry of biomolecules; for example, when dealing with protein molecules, often only the symmetry of the main strand of the peptide bonds is considered, irrespective of the differing side groups.

Asymmetric unit. Contiguous smallest building block that is symmetrically repeated.

Repeating unit (constitutional repeating unit). Smallest repeating chemical building block.

According to the *equivalence postulate* (equivalence principle) of polymer chemistry, the repeating unit and the asymmetric unit generally are considered to be equivalent, even if there are differences in the conformations of side chains (De Rosa & Auriemma, 2013; Natta & Corradini, 1959). However, there do exist cases

[1] The original paper is written in German because I can express my ideas in a most accurate way only in my mother tongue. This is an anticipation of how scientific papers are likely to be published in the coming future. We already have computer programs that can translate a text. For the time being, the quality of the translations is still deficient, but the quality is improving. Up to the 1970s computer scientists were convinced that it would be impossible to create a computer program capable of playing chess. In the same way, it was 'clearly evident' that it is technically unfeasible to produce a mobile telephone, the location of which can be spotted anywhere on any continent within a few seconds.
It is to be expected that computer programs will become available that produce nearly flawless translations. Just as a human translator cannot translate a crystallographic text unless he or she has knowledge in crystallography, the coming translation programs will be special, self-learning programs dedicated to some specific field(s) of science. Once it requires only a click to select this field and in what language we want to read or hear a text, hardly any scientist-to-be will ever again want to take the huge effort to learn a foreign language. For many scientists, an aversion against learning languages has strongly influenced the choice of their profession. Scientists will feel unburdened from having to struggle with the complicated and often illogical semantics, syntax, grammar and spelling of an alleged *lingua franca* of science that is not their native language.

where the repeating unit and the asymmetric unit definitely cannot be considered to be equivalent.

We do not use the expressions 'monomer' or 'monomeric unit'. The repeating unit indeed is often identical with a monomeric unit; however, in a molecule like polyethylene the repeating unit is CH_2 while the chemical monomer is C_2H_4. In a polyamide consisting of a dicarbonic acid and a diamine there are two 'monomers', and the repeating unit is –NH–CO–$(CH_2)_x$–CO–NH–$(CH_2)_y$–. The repeating unit can be a single atom.

Translation period (translational repeating distance, translational identity period). Length along a straight line, after which the pattern of atoms is repeated congruently without a mutual rotation.

Spiral, coil. *Continuous*, spirally wound line. We only use this term for a cylindrical spiral that winds at a constant distance around a straight **spiral axis**.

Helix, helical chain. Polymeric molecule whose repeating units are located at symmetrically equivalent positions on virtual spirals, at least to a good approximation. For every atom of the asymmetric unit there is one spiral; all spirals have the same translation period.

Multiple helix. Several symmetry-equivalent helices that are interlocked and wind around the same spiral axis. We do not use this term for a helix whose coil for its part is wound up to a coil with a larger diameter.

Right hand rotation. On rotation about the *z* axis of a right-handed *xyz* coordinate system we move on the shortest path (rotation angle <180°) from the *x* to the *y* axis. A helix or screw axis is right handed if, upon a right hand rotation, we advance in the positive direction of the *z* axis. Frequently, right and left are perceived 'the wrong way around' as compared to a steering wheel. We rotate the steering wheel to the left to make a left turn. If we draw the *x* and *y* axis of a coordinate system on a sheet of paper as accustomed in mathematics, such that the *z* axis points at us, the direction defined as a right hand rotation corresponds to what we perceive as a left hand rotation of the steering wheel. To be correct, the *z* axis must point in the direction of motion.

3. Rod groups

The symmetry of a chain-like molecule which has translational symmetry in only one preferential direction is designated by a rod group. There exist no Schoenflies symbols for rod groups. The Hermann-Mauguin symbols correspond to those of the space groups, but they begin with a script style $\wp$. Rod groups with rotation axes and screw axes of the orders 1, 2, 3, 4 and 6 (crystallographic rod groups) have been compiled in *International Tables for Crystallography* (2010), Volume E; they also can be looked up at the Bilbao Crystallographic Server, www.cryst.ehu.es. In a rod group, the order of a symmetry axis in the preferential direction is not restricted to the mentioned numbers. Generally, the preferential direction is chosen to be **c**; if **a** or **b** are chosen, this can be designated by $\wp_a$ or $\wp_b$. A table of the Hermann-Mauguin symbols of non-crystallographic rod groups of any order can be found in the 6th edition of *International Tables for Crystallography* (2016), Volume A, Table 3.2.4.1.

For helices, only rod groups having screw axes along the spiral axis are to be considered: $\wp 2_1$, $\wp 3_1$, $\wp 3_2$, $\wp 4_1$ *etc*., or, generally, $\wp N_q$ with $q < N$ and $N > 1$ being an integer. Additionally, twofold rotation axes can be present perpendicular to the spiral axis; the corresponding symbols are $\wp 222_1$, $\wp 3_1 2$, $\wp 3_2 2$, $\wp 4_1 22$ *etc*., in general $\wp N_q 2$ (N odd ≥3) or $\wp N_q 22$ (N even ≥4). If N is odd, the symbol usually obtains an additional 1, for example $\wp 3_1 12$ or $\wp 3_1 21$, to indicate the orientation of the helix relative to the crystal lattice. Instead of $\wp 2_1$, usually the complete symbol $\wp 112_1$ is stated (2_1 axis in the direction of **c** = translational direction). $\wp 112$ has a rotation axis in the translational direction **c**; $\wp 211$ and $\wp 121$ have rotation axes perpendicular to **c**, but none in the direction of **c**. Many polymers with symmetries of this kind are known, for example, $\wp 8_3$ for polyisobutene or $\wp 10_3 22$ for polymeric sulfur.

Table 1
Maximal crystallographic rod subgroups of rod groups ρN_q, depending on the divisors of the number N. Take that modulo number with the smallest value ≥ 0; if the result is zero, a rotation axis is meant.

divisors of N	Maximal subgroups
6, 4	$\rho 6_{q \bmod 6}$, $\rho 4_{q \bmod 4}$
6	$\rho 6_{q \bmod 6}$
4, 3, $\neq 6$	$\rho 4_{q \bmod 4}$, $\rho 3_{q \bmod 3}$
4	$\rho 4_{q \bmod 4}$
3, 2, $\neq 6$	$\rho 3_{q \bmod 3}$, $\rho 2_{q \bmod 2}$
3, $\neq 6$	$\rho 3_{q \bmod 3}$
2, $\neq 4$, $\neq 6$	$\rho 2_{q \bmod 2}$
$\neq 2$, $\neq 3$	$\rho 1$

Table 2
Examples for possible crystallographic rod subgroups of a few rod groups. In addition to the listed further subgroups there are infinite many isomorphic subgroups (with increased translation period).

rod group	maximal subgroups	further subgroups
$\rho 18_7$	$\rho 6_{7 \bmod 6} \rightarrow \rho 6_1$	$\rho 3_1$; $\rho 112_1$; $\rho 1$
$\rho 24_9$	$\rho 6_{9 \bmod 6} \rightarrow \rho 6_3$; $\rho 4_{9 \bmod 4} \rightarrow \rho 4_1$	$\rho 3$; $\rho\ 112_1$; $\rho 1$
$\rho 16_7$	$\rho 4_{7 \bmod 4} \rightarrow \rho 4_3$	$\rho 112_1$; $\rho 1$
$\rho 12_4$	$\rho 6_{4 \bmod 6} \rightarrow \rho 6_4$; $\rho 4_{4 \bmod 4} \rightarrow \rho 4$	$\rho 3_1$; $\rho 112$; $\rho 1$
$\rho 9_5 2$	$\rho 3_{5 \bmod 3} 2 \rightarrow \rho 3_2 2$	$\rho 3_2$; $\rho 211$; $\rho 1$
$\rho 7_4 2$	$\rho 211$	$\rho 1$
$\rho 10_3 22$	$\rho 222_{3 \bmod 2} \rightarrow \rho 222_1$	$\rho 112_1$; $\rho 211$; $\rho 121$; $\rho 1$
$\rho 4_2 22$	$\rho 4_{2 \bmod 4} \rightarrow \rho 4_2$; $\rho 222$	$\rho 112$; $\rho 211$; $\rho 121$; $\rho 1$

The rod-site symmetry of a polymeric molecule in a crystal has to be a crystallographic subgroup of the rod group of the free molecule. The possible subgroups are easy to determine. If the rod group of the molecule is ρN_q and N has the divisors 6, 4, 3 or 2, then they are the maximal crystallographic subgroups that are obtained from Table 1, and, in addition, their subgroups. The maximal subgroups of the rod groups $\rho N_q 2$ (N odd) and $\rho N_q 22$ (N even) follow from the maximal subgroups listed in Table 1 by appending the two(s) or, in the case of $\rho 2_q$ and $\rho 1$, by inserting the two(s) after the ρ. The additionally possible rod subgroups of the rod groups determined this way can be looked up in *International Tables for Crystallography* (2010), Volume E. A few examples are given in Table 2.

In the crystal, the polymeric molecule adopts a rod-site symmetry, which is a rod subgroup of the space group. The rod-site symmetries are called *penetration rod groups* in *International Tables for Crystallography* (2010), Volume E, where they are a subject of Chapter 5, *Scanning of space groups*. A penetration rod group consists of that subset of the symmetry operations of the space group which leave invariant a traversing straight line, which in our case is the spiral axis. The penetration rod group depends on the direction and the location of the straight line relative to the space group; the location is specified by the coordinates of a point on the straight line. Every point in a space group has a site symmetry and it is one out of infinite many symmetry equivalent points. Accordingly, the traversing straight line is one out of infinite many symmetry equivalent lines, every one having the same symmetry of the penetration rod group.

Penetration rod groups have not been listed in *International Tables for Crystallography* nor, to my knowledge, anywhere else. Which rod subgroups are to be considered as penetration rod groups, however, can be disclosed by comparing the images of the symmetry elements of Volumes E and A.

4. Chemical designation for helical polymeric molecules

Polymeric chain molecules often adopt the shape of helices in the crystalline state. To be more exact: We imagine a spiral that runs through symmetry-equivalent atoms of the polymer molecule. The spiral is a continuous, coiled line having the rod group $\rho\infty_1 2$ or $\rho\infty_{-1} 2$, which is not really present in the molecule. Of course, chemists place the spiral along the polymer main chain.

In polymer chemistry, a helical polymer molecule is designated as a *N*/*r* helix. *N* is the number of repeating units per translation period and *r* is the number of the corresponding coil turns; *N* and *r* are positive integer numbers without a common divisor. In addition, the letters *P* (for plus; formerly *R*) or *M* (minus, formerly *S*) indicate if the spiral is right or left handed. For example, a 7/2-*P* helix has seven repeating units in two right-handed coil turns per translation period.

The number of repeating units *per coil turn* can be an irrational number. Every irrational number can be approximated by a fractional number *N*/*r*, the agreement being the better, the larger the numbers *N* and *r*. Experimentally determined numbers *N* and *r* are the less reliable, the larger they are, because they rely on decreasing reflection intensities of the X-ray experiment. In this case it is more reasonable to state the number *N*/*r* as a decimal number, such as it is common in protein chemistry. Small distortions of the molecules can render possible small numbers *N* and *r* (see Section 8).

Sometimes the symbols obtain additions, for example, **s**(7/2) in order to point out the helical structure or **s**(7/2)2 to indicate the presence of twofold rotation axes perpendicular to the spiral axis (De Rosa & Auriemma, 2013). The distinction of chiral pairs of *P* and *M* helices in the manner 7/2 for *P* and 7/5 for *M* (5 = 7 – 2), to be found in the literature, is rather unfortunate, because a 7/2 helix is something different than a 7/5 helix (one has two, the other one has five coil turns per translation period). The cause of the misunderstanding is that a *N*/*r* *P*-helix and a *N*/(*N* – *r*) *P*-helix have mirror-inverted screw axes; for example, the screw axis of a 7/2-*P* helix is 7_4, and that of a 7/5-*P* helix is 7_3. An unambiguous distinction would consist in using a negative *r* value for the *M* helix, for example 7/2 and 7/–2.

Generally, protein and nucleic acid molecules have no symmetry in the mathematical and crystallographic sense, since the amino acids or the nucleotides, as a rule, have no periodic sequence (collagen molecules are an exception). In a protein α-helix the main polypeptide chain $(\text{-CONH}_2\text{CH–})_x$ is reasonably rigid by means of hydrogen bridge bonds, with 3.6 peptide groups per coil turn (3.6 = 18/5). In nucleic acids the two strands of the double-strand are complementary to each other, but they are not symmetry equivalent, with 10 to 10.5 ribose phosphate units per coil turn. No *N*/*r* symbols can be assigned to nano tubes, as there is no polymer main chain.

5. Experimental restrictions

Organic polymers often do not crystallize well (in the crystallographic sense); the crystals contain numerous faults. As a consequence, the X-ray reflections are broad, blurred and partly superposed, and the structure determination becomes inaccurate and less reliable. The value of the lattice parameter *c* (direction of helix axis) sometimes depends on the observability of a few weak reflections. For example, it is not sure if polyoxymethylene $(CH_2O)_\infty$ should rather be described as a 9/5 or a 29/16 helix. The corresponding lattice parameter is $c \approx 1727.4$ pm = 9 × 191.9 pm and $c \approx 5571.0$ pm = 29 × 192.1 pm, respectively, and the numerical values of 9/5 = 1.80 and 29/16 = 1.8125 repeating units per coil turn differ only marginally. In this case, a few very weak reflections seem to favour a 29/16 helix (Tashiro *et al*., 2007).

If the helices have no bulky side groups, their surface is more or less ‘smooth’. In that case the packing of the helices in the crystal often corresponds to a pseudohexagonal rod packing. A common consequence is misorder, especially random occurrence of *P* and *M* helices and helices mutually shifted in parallel. In such cases, no space groups can be stated. In this regard, inorganic compounds tend to be more ‘orderly’.

6. Polymer nomenclature and Hermann-Mauguin symbols

Fig. 1 shows a section of the crystal structure of tin iodide phosphide SnIP (Pfister *et al*., 2016). The structure contains helical polyphosphide ions $(P^-)_\infty$. A second helix $(SnI^+)_\infty$, consisting of alternating tin and iodine atoms, winds around every one of these $(P^-)_\infty$ ions. The $(P^-)_\infty$ as well as the $(SnI^+)_\infty$ helix is a 7/2 helix. The number of *P* and *M* helices in the crystal is equal; the crystal is racemic. Fig. 1 shows a *P* helix.

The translation vector **c** has been included in Fig. 1; it marks the direction and the unit length of the *z* axis. The numbers next to the atoms refer to the *z* coordinates (heights) of the atoms.

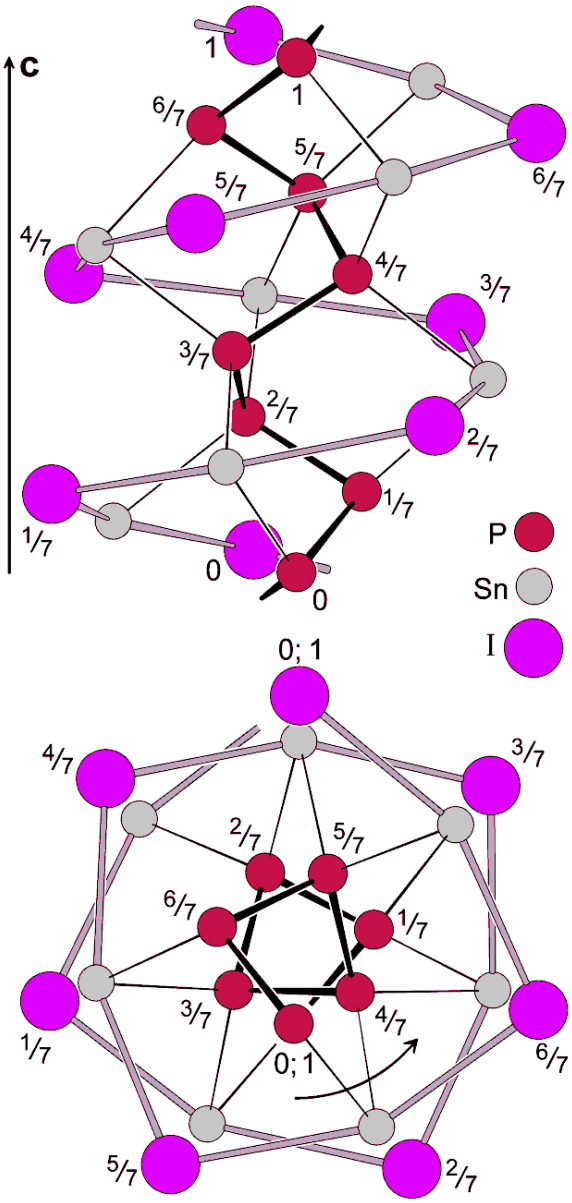

Figure 1
7/2-*P* helices in SnIP. Top: side view. Bottom: top view against the screw axis. One SnI strand surrounds one polyphoshide strand. Numerical values are the heights of the atoms (*z* coordinates), given as fractions of one translation length. Mean bond lengths: P–P 220 pm; Sn–P 269 pm; Sn–I 316 pm.

The $(P^-)_\infty$ strand contains seven phosphorus atoms in two coil turns; these are two turns amounting to 2 × 360° = 720°. From one P atom to the next the turning angle is 720°/7 ≈ 102.86°. Starting from an atom at the height $z_0 = 0$ and following the strand of the covalent bonds, we reach the next atom at a height of $z_0 + 1/7$ and after seven atoms we approach the height of $z_0 + 7/7 = 1$, which corresponds to one complete translation period. The same is valid for the atoms in the $(SnI^+)_\infty$ helix.

Having $N = 7$ repeating units per translation period, the symmetry axis has an order of seven; after each turn of 360°/7 there is a symmetry-equivalent group of atoms. To derive the Hermann-Mauguin symbol of a screw axis, we start from an atom at the height $z_0 = 0$ and perform a right turn by 360°/7 (turning arrow in the lower part of Fig. 1); we determine what is the height *z* of the symmetry equivalent atom in this position. As can be seen in the figure, this is at $z = 4/7$ in the case of the *P* helix. The Hermann-Mauguin symbol of the screw axis then is 7_4 and the rod group is $p7_42$ for the single $(P^-)_\infty$ helix, for the $(SnI^+)_\infty$ helix and for the ensemble of both helices. The 2 in the symbol of the rod group marks the presence of twofold rotation axes perpendicular to the spiral axis.

When determining the Hermann-Mauguin symbol N_q in the described manner, the following rules apply: Starting from an atom at the height $z_0 = 0$, we look for the *z* coordinate ($0 < z < 1$) of the symmetry-equivalent atom at the position turned by +360°/*N*. This *z* coordinate is noted as a fractional number *q*/*N*, and its numerator is the subscript number *q* of the Hermann-Mauguin symbol. The fraction must not be reduced. If *N* and *q* have a common divisor, the screw axis contains a rotation axis with the order of this common divisor. A 6_2 axis contains a twofold rotation axis, a 15_6 axis contains a threefold rotation axis.

In symmetry, a N_q screw axis is considered to be right handed if $q < ½N$ and left handed if $q > ½N$. A 7_4 screw axis is identical with a 7_{-3} screw axis (the atom at $z = 4/7$ is translationally equivalent to an atom at $z = -3/7$). By convention, only positive numbers are used in Hermann-Mauguin symbols, with $q < N$ and *N*, *q* = positive integers. N_q and N_{N-q} are the symbols for a pair of mirror-inverted (enantiomorphic) screw axes.

If we refer to a left-handed coordinate system when deriving the Hermann-Mauguin-Symbol, or, equivalently, if we perform a left turn, we arrive at an atom at $z = 3/7$ (Fig. 1). That is the nearest symmetry-equivalent atom after a rotation by ±360°/7.

The right handed 7/2 *P*-helix has the symmetry of a left handed screw axis 7_4. The very

same helix is simultaneously right and left handed? Yes, that is so, and it has to do with the point of view. If our helix were a continuous spiral, this would not be possible. Our helices, however, consist of atoms or discrete points, and the spirals exist only in our imagination. We have inserted them in two different ways:

(1) One the one hand, we followed the strand of covalent bonds and derived the symbol 7/2-*P*. That is the chemical point of view. We continue along the yellow spiral in Fig. 2, which we call the *chemical spiral*.

(2) On the other hand, we looked for the *z* coordinate of the nearest symmetry-equivalent atom after a rotation by 360/7°. It is situated after a left turn at $z = {}^{3}/_{7}$, and the screw axis symbol is 7_4. That is the point of view of symmetry. We continue along the dark green spiral in Fig. 2, which we call the *symmetry spiral*.

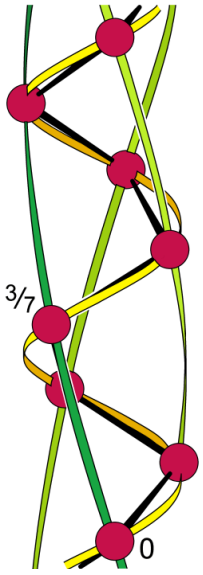

Figure 2
One translation period of the polyphosphide strand in SnIP with inserted spirals (same view as in Fig. 1, top). Yellow: right-handed spiral which follows the covalent bonds of the 7/2-*P* helix. Green: three interlocked symmetry spirals which follow the course of the left-handed 7_4 screw axis.

If *c* is the translation period, the dark green spiral in Fig. 2 has a translation period of 3*c*. Since there is a symmetry equivalent position after every translation by *c*, we have a total of three symmetry equivalent green spirals in Fig. 2. The number of interlocked symmetry spirals is always equal to the subscript number *q* in the Hermann-Mauguin symbol N_q. If $q < ½ N$, these are *q* right-handed symmetry spirals with a translation period of *qc*. If $q > ½ N$ there are either *q* right-handed symmetry spirals with a translation period of *qc* or $N - q$ left-handed symmetry spirals with a translation period of $(N - q)c$. Every single symmetry spiral continues along an N_1 or N_{N-1} screw axis, respectively, with the mentioned translation period.

If $q = ½N$, there are *q* left and *q* right handed symmetry spirals, and the screw axis itself is not chiral. Nevertheless, the chemical helix is chiral (provided there are no mirror or glide planes and no points of inversion or rotoinversion)

We draw covalent bonds as bond lines between the atoms according to chemical considerations. What is the chemical spiral depends on where we draw the covalent bonds. For symmetry considerations covalent bonds do not exist and are completely irrelevant. The situation is similar to drawing a left-handed spiral with a thin paintbrush onto the thread of a right-handed screw; paint points appear on the ridge of the thread where the painted spiral crosses the thread; the points simultaneously belong to the thread and the painted spiral.

The *N*/*r* symbols of polymer chemistry can easily be converted to the corresponding Hermann-Mauguin symbols N_q. The conversion formula is (Spruiell & Clark, 1980):

$$n\,N \pm 1 = r\,q$$

where $n = 0, 1, 2, \ldots$ and $0 < q < N$. + applies to *P* helices, – to *M* helices. For a 7/2 helix ($N = 7$, $r = 2$) this is:

$$1 \times 7 + 1 = 2 \times 4 \text{ for } P, \rightarrow 7_4$$
$$1 \times 7 - 1 = 2 \times 3 \text{ for } M, \rightarrow 7_3$$

If $r = 1$, then $q = 1$ or $q = N - 1$. The formula is not applicable to multiple helices. In addition, it is assumed that all repeating units of the helix are symmetry equivalent, *i.e.* the asymmetric unit and the repeating unit are supposed to be identical. Results for small values of *r* are summarized in Table 3.

Table 3
Hermann-Mauguin symbols N_q for N/r helices with small values of r. n = arbitrary positive integer; only combinations of N and r with no common divisor.

N	r	q	
		P helix	M helix
n	1	1	$N-1$
$2n+1$	2	$\frac{1}{2}(N+1)$	$\frac{1}{2}(N-1)$
$3n-1$	3	$\frac{1}{3}(N+1)$	$\frac{1}{3}(2N-1)$
$3n+1$	3	$\frac{1}{3}(2N+1)$	$\frac{1}{3}(N-1)$
$4n-1$	4	$\frac{1}{4}(N+1)$	$\frac{1}{4}(3N-1)$
$4n+1$	4	$\frac{1}{4}(3N+1)$	$\frac{1}{4}(N-1)$
$5n-2$	5	$\frac{1}{5}(3N+1)$	$\frac{1}{5}(2N-1)$
$5n-1$	5	$\frac{1}{5}(N+1)$	$\frac{1}{5}(4N-1)$
$5n+1$	5	$\frac{1}{5}(4N+1)$	$\frac{1}{5}(N-1)$
$5n+2$	5	$\frac{1}{5}(2N+1)$	$\frac{1}{5}(3N-1)$
$6n-1$	6	$\frac{1}{6}(N+1)$	$\frac{1}{6}(5N-1)$
$6n+1$	6	$\frac{1}{6}(5N+1)$	$\frac{1}{6}(N-1)$

A unique calculation is not possible in the opposite direction, from the Hermann-Mauguin symbol N_q to the N/r symbol, because it depends on where the covalent bonds are assumed to exist. In addition, a 7/9, 7/16 and every other 7/(2 modulo 7) *P*-helix as well as every 7/(5 modulo 7) *M*-helix has a 7_4 screw symmetry. The situation is similar to the point groups: it is possible to deduce the point group from the molecular structure, but not contrariwise.

Hermann-Mauguin symbols have been existing since 1928; the symbols for helices have been utilized in polymer chemistry since the 1960s. There had been no complications with the terminology until the International Union for Pure and Applied Chemistry published the new *IUPAC Recommendations 2011: Definitions and terms relating to crystalline polymers* (Meille *et al*., 2011). Now the recommendation is: "The helix symbol M_N denotes the integer number of helix residues (M) and helical coil windings (helical turns), (N), approximated by the sequence of bonds along the polymer main chain in a chain identity period. A helix with M helix residues in N turns can be denoted an M_N helix." According to that, a 7/2 helix should now be termed a 7_2 helix. The 7_2 looks like a Hermann-Mauguin symbol and is confused with it; however, the Hermann-Mauguin symbol for a 7/2 helix actually is 7_3 or 7_4, depending on chirality.

The definition of the Hermann-Mauguin symbols is clearer and unique, but they only specify symmetry. The symbols of polymer chemistry are more convenient for chemists; they refer to the chemical structure, but they depend on how we regard the course of a spiral. As a rule, chemists will follow the course of the covalent bonds of the polymer main chain; therefore, the course of the spiral depends on where we draw the covalent bonds between the atoms. The measure for this are the interatomic distances as compared to known bond lengths; the interatomic distances depend on the metrical conditions (length of the translation period, distance of an atom from the spiral axis and arrangement of the polymer chain atoms in the repeating unit). This will hardly ever cause doubts when dealing with organic polymers, but with regard to inorganic solids this is not always clear. Are the Sn–I bonding lines in Fig. 1 covalent bonds or not? Compared to the sums of the covalent radii (Cordero *et al*., 2008; Pyykkö & Atsumi, 2009), the P–P bond length is inconspicuous, the Sn–P length is slightly longer (269 instead of 251 pm) and Sn–I is substantially longer (316 instead of 273 pm).

Other building blocks in lieu of covalent bonds can also serve to describe the course of a chemical spiral, for example, coordination polyhedra. At the example of $PPh_4[Cu_3I_4]$ we will rely on joined coordination tetrahedra (see Section 8).

Table 4 presents an arbitrary selection of helical polymers. More can by found at De Rosa & Auriemma (2013).

Table 4

Examples of structures with helical molecules (arbitrary selection).

Meanings in the column of the chemical helix symbol: *R*, racemate; 2×, double helix; 3×, tripe helix; *c*′, translation period of the multiple helix; 2*c*′, 3*c*′, ... translation period of the single helix.

compound	repeating unit	chemical helix	rod group	penetrat. rod group	space group	references
isotactic polypropene-α2	CH_2–CHMe	3/1-*R*	$\rho 3_1 + \rho 3_2$	$\rho 1$	$P2_1/c$	Hikosata & Seta (1973)
polyisobutene	CH_2–CMe_2	8/3-*P*	$\rho 8_3$	$\rho 1\,1\,2_1$	$P2_12_12_1$	Tanaka *et al.* (1974), Immirzi *et al*. (2007)
isotactic polystyrene	CH_2–CHPh	3/1-*R*	$\rho 3_1 + \rho 3_2$	$\rho 3_1 + \rho 3_2$	$R3c$	Natta & Corradini (1955, 1960)
isotactic poly-*o*-methylstyrene	CH_2–CH-*o*-C_6H_4Me	4/1-*R*	$\rho 4_1 + \rho 4_3$	$\rho 4_1 + \rho 4_3$	$I4_1cd$	Corradini & Ganis (1960)
isotactic poly-*m*-methylstyrene	CH_2–CH-*m*-C_6H_4Me	11/3-*R*	$\rho 11_4 + \rho 11_7$	$\rho 1$	$P\bar{4}$	Corradini & Ganis (1960)
isotactic poly-4-methyl-1-pentene-II	CH_2–$CHCH_2CHMe_2$	7/2-*R*	$\rho 7_3 + \rho 7_4$	$\rho 1$	$P\bar{4}b2$	Kusanagi *et al*. (1978)
polytetrafluoro-ethene-II	CF_2	13/6 †	$\rho 13_11 2$	?	pseudo-hexagonal	Clark (1999)
polytetrafluoro-ethene-IV	CF_2	15/7	$\rho 15_2 2$	ca. $\rho 3_221$	pseudo-hexagonal	Clark (1999)
polyoxymethylene	O–CH_2	9/5-*M* or 29/16-*M*	$\rho 9_7$ or $\rho 29_9$	$\rho 3_1$ or $\rho 1$	$P3_1$ or $P1$	Tashiro *et al*. (2007)
isotactic poly-*t*-butylethyleneoxide	O–CH_2–$CHCMe_3$	9/4-R	$\rho 9_2 2 + \rho 9_7 2$	$\rho 1\,2\,1$	$P\bar{4}n2$	Sakakihara *et al*. (1973)
α-poly-L-lactide	CH_2–CHMe–COO	10/3-*P*	$\rho 10_722$	$\rho 1\,1\,2_1$	$P2_12_12_1$	Alemán *et al*. (2001)
polyethylene-imine	NH–CH_2–CH_2	2× 5/1-*R* 2*c*′	$\rho 10_422 + \rho 10_622$	$\rho 2\,2\,2$	*Fddd*	Chatani *et al*. (1982)
polysulfur	S	10/3-*R*	$\rho 10_322$ $\rho 10_722$	$\rho 1\,2\,1$	$P121$	Lind & Geller (1969)
polysulfur-II; selenium-II	S; Se	4/1-*R*	$\rho 4_122 + \rho 4_322$	$\rho 4_122 + \rho 4_322$	$I4_1/acd$	Fujihisa *et al*. (2004)
selenium; tellurium	Se; Te	3/1-*P*	$\rho 3_121$	$\rho 3_121$	$P3_121$	9 determinations, 1924–1993
SnIP	SnI^+ and P^-	7/2-*R*	$\rho_a 7_32 + \rho_a 7_42$	$\rho_a 1\,2\,1$	$P12/c1$	Pfister *et al*. (2016)
$K_2P_2Se_6$	$P_2Se_6^{2-}$	3/1-*P*	$\rho 3_121$	$\rho 3_121$	$P3_121$	Chung *et al*. (2007)
3-aminomethyl-pyridino-silver-perchlorate	$(AgNC_5H_4CH_2NH_2^+)_2$ 2 repeating units per asymmetric unit	3× 2/1-*R* 3*c*′	$3\times \rho_b 1\,2_11$	$\rho_b 1\,2_11$	$P12_1/c1$	Sailaja & Rajasekharan (2000)
[Ag-5,6-chiragene-1,5-dimethyl-naphthyl]PF_6	$AgC_{46}H_{44}N_4^+$	2× 6/1-*P* 2*c*′	$\rho 6_222$	$\rho 6_222$	$P6_222$	Mamula *et al.* (1999)
$PtCl_3$; $PtBr_3$ = $[Pt_6X_{12}] \cdot 6PtX_4$	PtX_4, edge-sharing octahedra	3/1-*R*	$\rho 3_121 + \rho 3_221$	$\rho 3_1 + \rho 3_2$	$R\bar{3}$	v. Schnering *et al*. (2004)
$PPh_4[Cu_3I_4]$	$Cu_{0.75}I^-$, face-sharing tetrahedra	8/3-*R*	$\rho_a 8_322 + \rho_a 8_522$	$\rho_a 2_122$	*Ccce*	Hartl *et al*. (1994)

† incommensurate, 13/6 fulfilled approximately, more exactly 54/25 or 473/219 or 948/439

7. Multiple helices

The chemical helix symbol *N*/*r* designates the shape of a *single* helix. When several symmetry-equivalent helices are interlocked with each other, this has to be reported separately in an appropriate way. What is the symmetry of the ensemble of the helices depends on how many single chemical helices are involved and how they are mutually rotated.

No simple formula can be specified to convert the chemical helix symbol to the Hermann-Mauguin symbol of the multiple helix. The formulas of Table 5 can be used for some cases; Table 5 does not cover all possibilities. The formulas can be applied repeatedly; two doublings yield a quadrupled helix. Chemically insensate, colliding or mutually interleaving helices can result in some cases with certain numerical combinations, depending on the arrangement of the atoms in the repeating unit.

Example: A 9/5-*P* helix has a 9_2 screw axis according to Table 3 (q = 2). Two (Z = 2) of these helices, combined without mutual rotation ($\varphi = 0°$) and shifted by s = ½**c**, according to formula (1) of Table 5 result in a double helix with the screw symmetry 9_4 and a halved translation period **c**′ = ½**c.** Two of these double helices, mutually rotated by 180° and once again shifted by ½**c**′, yield a quadruple helix, which, according to formula (7), has an 18_{13} screw axis and an unchanged translation period ½**c**. This quadruple helix consists of four 9/5-*P* helices, being mutually rotated by 180° and shifted by ¼**c**.

Figure 3 shows helices with 14-fold symmetry. All depicted helices that have the same Hermann-Mauguin symbol have exactly the same arrangement of their repeating units. The only difference between the images consists in where bonds have been drawn between the repeating units. As can be seen, this can mean rather different chemical helices, some being interlocked to multiple helices. In each case, the bond lines of the first image depicted for a Hermann-Mauguin symbol show the corresponding symmetry spiral(s).

The chemical helical structure of a multiple helix is not always expressed by its Hermann-Mauguin symbol. For example, a triple helix consisting of three interlocked 3/1 helices, each one with $p3_1$ symmetry, may have the symmetry $p3$ with a threefold rotation axis.

Table 5

Determination of the Hermann-Mauguin screw axis symbol $N'_{q'}$ of a multiple helix, consisting of Z equidistant, symmetry-equivalent chemical single helices N/r, each with a N_q screw axis.
m, n = arbitrary integer; φ = turning angle from one to the next helix accompanied by a shift of the helix by s parallel to **c**; **c** = translation vector of the single helix; **c′** = translation vector of the multiple helix; d = common divisor of Z and N; the value of q' is to be selected according to $0 \le q' < N'$ from the series of the modulo numbers; if $q' = 0$, a rotation axis is meant.

Z	N	φ	s	c′	N'	q'	formula Nr.
m †	n	0°	$\frac{1}{Z}\mathbf{c}$	$\frac{1}{Z}\mathbf{c}$	N	$(Zq) \bmod N'$	(1)
$2m+1$	Z	180°	$\frac{1}{2Z}\mathbf{c}$	$\frac{1}{Z}\mathbf{c}$	$2N$	N	(2)
m †	n	$\frac{360}{ZN}$ °	$(\frac{1}{Z}+\frac{q}{ZN})\mathbf{c}$	**c**	ZN	$N+q$, only $q < ½N$	(3a)
			$(\frac{1}{Z}-\frac{N-q}{ZN})\mathbf{c}$	**c**	ZN	$(Z-2)N+q$, only $q > ½N$	(3b)
m †	n	$-\frac{360}{ZN}$ °	$(\frac{1}{Z}-\frac{q}{ZN})\mathbf{c}$	**c**	ZN	$(Z-1)N+q$, only $q < ½N$	(4a)
			$(\frac{1}{Z}+\frac{N-q}{ZN})\mathbf{c}$	**c**	ZN	q, only $q > ½N$	(4b)
2	$2n$	180°	0	$\frac{1}{2}\mathbf{c}$	N	$(2q) \bmod N'$	(5)
2	$2n+1$	180°	0	**c**	$2N$	$[(N+1)q] \bmod N'$	(6)
2 ‡	$2n+1$	180°	$\frac{1}{2}\mathbf{c}$	**c**	$2N$	$[(N+1)q - N] \bmod N'$	(7)
3	$3n-1$	120°	0	**c**	$3N$	$[(N+1)q] \bmod N'$	(8)
3	$3n$	120°	0	$\frac{1}{3}$ c	N	$(3q) \bmod N'$	(9)
3	$3n+1$	120°	0	**c**	$3N$	$[(2N+1)q] \bmod N'$	(10)
4	$4n-1$	90°	0	**c**	$4N$	$[(N+1)q] \bmod N'$	(11)
4	$2n$	90°	0	$\frac{1}{d}\mathbf{c}$	$4N/d$	$[(N+d)q] \bmod N'$	(12)
4	$4n+1$	90°	0	**c**	$4N$	$[(3N+1)q] \bmod N'$	(13)
5	$5n-2$	72°	0	**c**	$5N$	$[(3N+1)q] \bmod N'$	(14)
5	$5n-1$	72°	0	**c**	$5N$	$[(N+1)q] \bmod N'$	(15)
5	$5n$	72°	0	$\frac{1}{5}\mathbf{c}$	N	$(5q) \bmod N'$	(16)
5	$5n+1$	72°	0	**c**	$5N$	$[(4N+1)q] \bmod N'$	(17)
5	$5n+2$	72°	0	**c**	$5N$	$[(2N+1)q] \bmod N'$	(18)
6	$6n-2$	60°	0	$\frac{1}{2}\mathbf{c}$	$3N$	$[(N+2)q] \bmod N'$	(19)
6	$6n-1$	60°	0	**c**	$6N$	$[(N+1)q] \bmod N'$	(20)
6	$3n$	60°	0	$\frac{1}{d}\mathbf{c}$	$6N/d$	$[(N+d)q] \bmod N'$	(21)
6	$6n+1$	60°	0	**c**	$6N$	$[(5N+1)q] \bmod N'$	(22)
6	$6n+2$	60°	0	$\frac{1}{2}\mathbf{c}$	$3N$	$[(2N+2)q] \bmod N'$	(23)

† m and r without common divisor
‡ $r = 2m$.

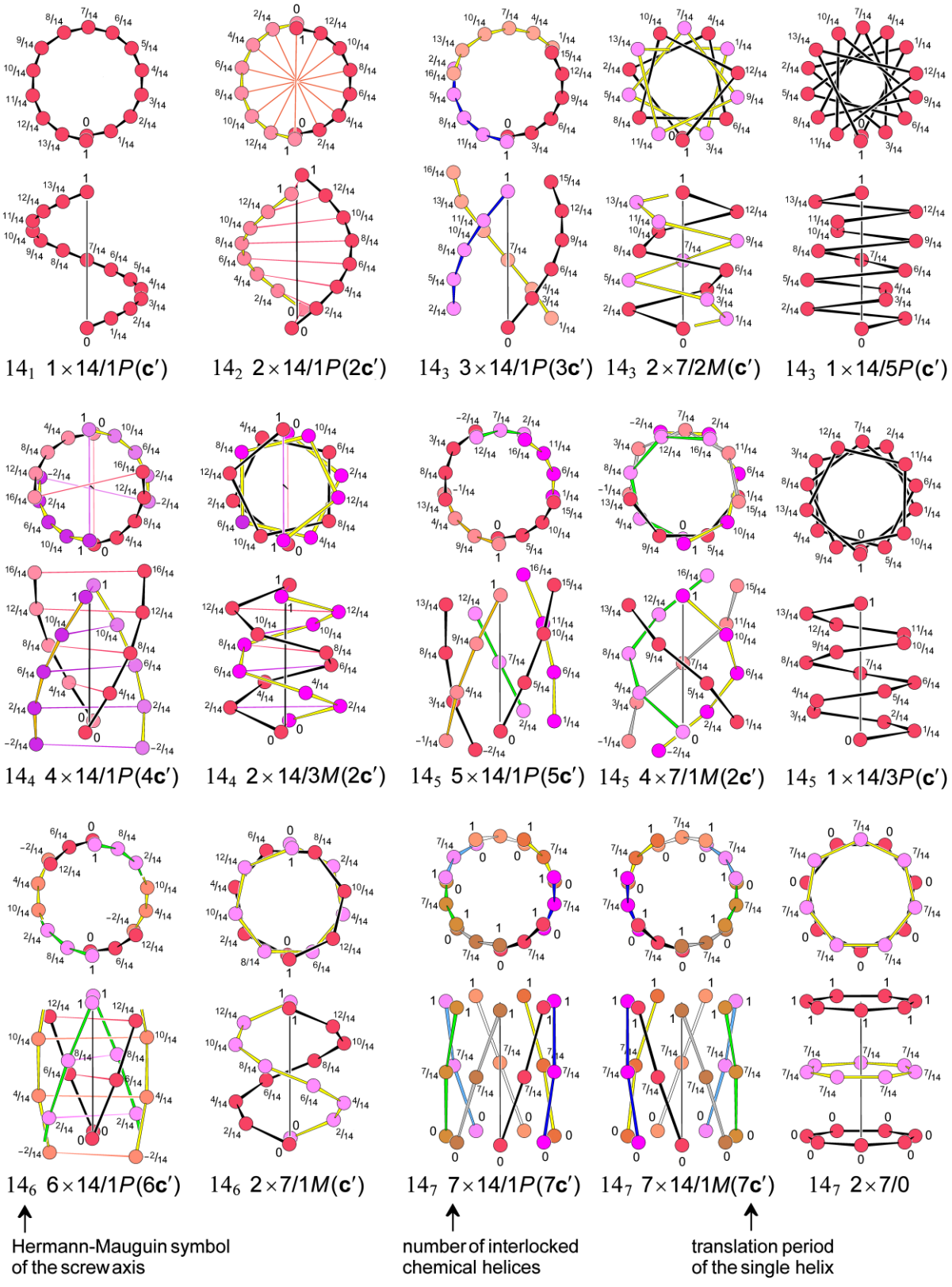

Figure 3
Helices with 14-fold screw axes. Each sphere represents one repeating unit that may consist of an asymmetric arrangement of atoms. Spheres and bonding lines of the same color belong to one chemical helix. The only difference between helices of the same Hermann-Mauguin symbol is where bonding lines have been drawn.

8. Coordination polyhedra as repeating units

Inorganic structures are often being described with the aid of joined coordination polyhedra. For example, tetrahalides often form chains of edge-sharing octahedra. The chains are helical for certain configurations (Müller, 1981). Chains of this kind occur as 3/1 helices in $PtCl_3$, which is a mixed-valence compound, consisting of Pt_6Cl_{12} clusters and $(PtCl_4)_\infty$ helices (von Schnering *et al*., 2004).

A helical structure does not necessarily have translational symmetry. In that case, it does not have a Hermann-Mauguin symbol nor a translation period. For example, the Boerdijk-Coxeter helix (also called tetrahelix) is a mathematically constructed helix consisting of regular, face-sharing tetrahedra. The calculated turn angle from one tetrahedron to the next is arc cos (–⅔) ≈ 131.81° (Boerdijk, 1985; Buckminster-Fuller, 1975; Coxeter, 1985). That is an irrational number, which means that the translation period of the helix is infinite. This irrational number can be approximated by fractional numbers of the kind $r \times 360°/N$ (r = number of coil turns, N = number of tetrahedra), for example, $3 \times 360°/8 = 135.0°$ or $26 \times 360°/71 = 131.83°$. With a corresponding size of the unit cell such a strand of tetrahedra can be fitted into a crystal within the limits of experimental accuracy. In addition, chemical structures are sufficiently flexible to adapt themselves to the crystallographic restraints.

In fact, the Boerdijk-Coxeter helix has been observed in crystalline $PPh_4[Cu_3I_4]$, with slight distortions of the tetrahedra (Hartl & Mahdjour-Hassan-Abadi, 1994). The crystals are racemic and contain 8/3 helices, consisting of 8 coordination tetrahedra in 3 coil turns per translation period, with a mean turning angle of 135.0° from tetrahedron to tetrahedron (Fig. 4). The corresponding rod groups are (approximately) $\rho 8_3 22$ and $\rho 8_5 22$. The helices run along of 2_1 screw axes in the space group *Ccce* and fulfil the crystallographic rod-site symmetry $\rho_a 2_1 22$, which is a subgroup of $\rho 8_3 22$ and $\rho 8_5 22$. It is not possible to draw covalent Cu–I bonds, because the copper atoms are mobile within the strand of the tetrahedra, amounting to three copper atoms per four tetrahedra.

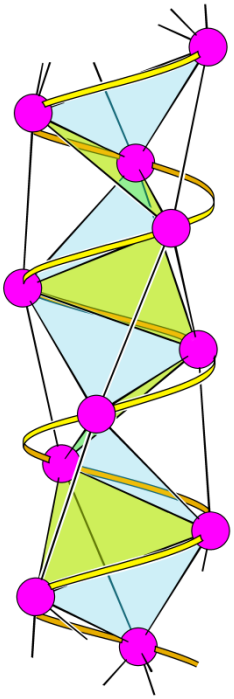

Figure 4
Section of a strand of face-sharing coordination tetrahedra in $PPh_4[Cu_3I_4]$. The copper atoms are not shown; they are mobile in between the tetrahedra, with three Cu atoms per four tetrahedra. Every tetrahedron has two faces alternately drawn in blue and green, which are shared with two neighbouring tetrahedra.

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